PROCESS FOR DISTILLATION AND DECARBONIZATION OF OIL SHALE SPECIES USING FLUIDIZED BED

FIELD OF THE INVENTION

The present invention relates to the coal chemical engineering field, directing to a process and a device for dry distillation and decarbonization of oil shale species using a fluidized bed.

BACKGROUND OF THE INVENTION

The oil shale, a kind of sedimentary rock, contains abundant organics. A ton of oil shale can produce at least 38L of shale oil, that is to say, oil shale contains 2-30% of shale oil. Recently, the studies around the world have shown that oil shale is a rich resource, but it has not been well utilized. It is estimated that about 3,000 billion barrels of raw oil are stored in the oil shale, and the raw oil is called as shale oil, among which only less than 200 billion barrels are utilized by the prior art.

Presently, it is much more expensive to extract oil from the oil shale than to purchase raw oil. Due to the problems in the exploitation technology, the fund and the environment, the oil extracted from the oil shale cannot completely replace the raw oil in the market of petrochemical fuel in the next dozens of years. Additionally, the inorganics (also known as the parent material of the oil shale) in the oil shale from different places of production varies a lot, and the most of the inorganics (parent material) is silicon-aluminum-oxide. After the organic matter and the carbon are removed, the parent material with high content of silicon and aluminum and low level of other impurities can be used as the carrier of catalyst, while other parent material with high content of impurities can be used as construction material.

Typically, the oil shale and coal gangue are associated minerals of coal, both of which are piled as garbage after being dug out with the coal. The piled oil shale or coal gangue occupies the land, and furthermore, it is easy to autoignite.

The coal gangue and the oil shale have many in common, but the coal gangue contains only a few organics and much carbon. Brown coal, peat coal, peat cube, etc. also comprise many organics, and therefore, after dry distillation, they produce coal tar which is similar to heavy crude.

The existing industrialized technology for processing oil shale is to grind the oil shale to be used as fuel for power generation or boiler furnace. The existing technology for extracting oil shale comprises the methods using solid heat carrier and that using gas heat

carrier. The main disadvantages of the technology using solid heat carrier to extract oil shale are the severe wear the device, the short cycle of the production, and the difficulty of energy recovery. The technology using gas heat carrier consumes much energy and causes dust pollution.

Some other existing technologies are mainly one-step methods of fluidizing combustion or recycling fluidizing combustion, which seldom utilize the parent material of oil shale.

Chinese Patent Application CN 91102884 discloses a process for removing and transforming the minerals in the oil shale, and the main content thereof is to pretreatthe oil shale with strong acid or alkali to improve its combustion performance and the chemical engineering availability. The main disadvantages of this patent application lie in that the use of strong acid and alkali during the process increases the danger of operation and causes some pollution to the environment, furthermore, it is merely a pretreatment process.

Chinese Patent Application CN 93102071 discloses a method for producing combustible gas from the inferior solid fuel such as the oil shale or other analogues. The technology in this patent application employs boiling bed process, the main disadvantages of which lie in that all of the shale oils are pyrolyzed into combustible gas, and therefore the aromatic compounds in the shale oil cannot be sufficiently recovered to give aromatic product with high added value or raw materials for petroleum chemical industry.

Because of the emergence of the petroleum crisis, the efforts to find new resources are extremely active. The solar energy, hydrogen energy, wind energy, tide energy and nuclear energy, etc. are under development or partly used.

In summary, presently there is still a lack of adequate energy supply in the world. Therefore, there is an urgent need in this field to develop new technologies of effectively utilizing oil shale species, especially the technologies of extracting liquid oil.

SUMMARY OF INVENTION

The objective of the present invention is to provide a method of effectively extracting liquid oil product from oil shale species with a low cost.

In the first aspect of the present invention, it provides a method of processing oil shale species, comprising the steps of:

(a) deoiling the powdered oil shale species by dry distillating in the fluidized bed reactor to produce oil gas and deoiled oil shale;

(b) recovering the resultant oil gas.

In another preferred example, the method further comprises the step of:

(c) decarbonizing the deoiled oil shale in the fluidized bed reactor in the presence of oxygen (15-35% V/V oxygen on the basis of the total gas), under the pressure of 0.1-0.6 MPa, the temperature of 500-800°C, and the volume ratio of the gas to solid of 1.0-20.0:1 V/V, thereby obtaining heat and deoiled and decarbonized oil shale.

In another preferred example, the average particle size of the oil shale species in the form of powder is about 50-500 micrometer, more preferably about 60-200 micrometer.

In another preferred example, the reaction condition in the step (a) is: the reaction pressure of 0.1-0.6 MPa, the temperature of 400-800 °C, and the volume ratio of the gas to solid of 1.0-20.0:1 V/V.

In another preferred example, the method further comprises the step of: fractionating the recovered oil gas to produce tower top gas, gasoline fraction, diesel oil fraction, coal pitch and heavy shale oil; and delivering the heavy shale oil back to the fluidized bed reactor for distillating and deoiling for recycled use.

In another preferred example, the method further comprises the step of: separating the resultant tower top gas to obtain the discharged dry gas, liquefied gas and condensate oil; and delivering the discharged dry gas in high temperature back to the fluidized bed reactor for distillating and deoiling for recycled use.

In another preferred example, the oil shale species includes: oil shale, coal, coal gangue, peat coat, peat cube, or the mixture thereof.

In another preferred example, the fluidized bed reactor in the steps (a) and (c) is selected from the group consisting of reactor riser, batch-type fluidization kettle reactor, bubbling-type fluidized bed reactor, and moving bed reactor.

In the second aspect of the present invention, it provides a device for processing the oil shale species, comprising:

(a) a fluidized bed reactor for distillating and deoiling, having an inlet of the oil shale species, an inlet of heavy shale oil, an inlet of high temperature dry gas, an outlet of oil gas, and an outlet of the deoiled oil shale;

(b) a fractionating tower, having a pipe and inlet associated with the oil gas outlet of the fluidized bed reactor for distillating and deoiling, and an outlet of fractions;

(c) a fluidized bed reactor for decarbonization, having an pipe and inlet

associated with the outlet of deoiled oil shale of the fluidized bed reactor for distillating and deoiling, an inlet of air, an outlet of flue gas, and an outlet of deoiled and decarbonized oil shale.

In another preferred example, the device further comprises (d) a gas separation tank, used to further separate the gas produced in the fractionating tower (c).

DESCRIPTION OF DRAWINGS

Fig.1 is a brief diagram illustrating the processing scheme of deoiling and decarbonization of the oil shale by using the fluidized bed according to the present invention.

Wherein, the meanings of the reference signs are as follows: 1-block oil shale, 2-two-stage crasher, 3-oil shale powder, 4-dry distillation reactor, 5-oil gas, 6-high temperature dry gas, 7-heavy shale oil, 8-deoiled oil shale, 9-flue gas, 10-decarbonization reactor, 11-high temperature air, 12-deoiled and decarbonized oil shale, 13-fractionating tower, 14-tower top gas, 15-gasoline fraction, 16-diesel oil fraction, 17-coal pitch, 18-discharged dry gas, 19-liquefied gas, 20-gas separation tank, 21-condensate oil.

DETAILED DESCRIPTION OF INVENTION

Through extensive and intensive investigations, the inventor of the present invention has simultaneously performed the dry distillation of the oil shale and pyrolysis of the heavy shale oil in the same reactor, and decarbonized the deoiled oil shale in another reactor. Thus, the obtained shale oil can be used to produce aromatic products, light oil for chemical industry and fuel gas with high added values. Furthermore, the exhaust gas containing sulfur and nitrogen is discharged after purification and energy recovery, therefore, it hardly causes environmental pollution. The energy recovery system not only provides energy to the system but also provides the excess energy to the outside.

The principle of the present invention is as follows: The shale oil contained in powdered oil shale in fluidizing condition is gasified by using high temperature dry gas and/or high temperature stream as heat carrier and fluidizing medium, meanwhile, dry gas dissolves some organics in oil shale, that is, fluidizing, dry distillating and deoiling. The powder which has removed shale oil is fluidized by high temperature air under oxygen-rich condition. The carbon in oil shale is combusted, i.e. fluidizing

decarbonization. A energy recovery system(i.e. the system of the flue gas turbine and the residue heat boiler)is set for the high temperature produced in the decarbonization reactor. After energy recovery and purification by removing compounds such as sulfide and nitrogen compounds, the flue gas is discharged.

The processing scheme of the present invention is described briefly as follows: The large block of oil shale is physically grinded, with the size distribution of the grinded particle controlled to make the average size be about 50-500 micrometers, more preferably about 60-200 micrometers (Typically, the particle size distribution of 95% or more particles is in the range of 1-1000 micrometers, preferably of 50-800 micrometers). The powdered oil shale is delivered into the dry distillation reactor, and the powdered oil shale is fluidizing distilled with steam and/or dry gas. Meanwhile, the heavy shale oil is delivered into the dry distillation reactor and pyrolyzed at a high temperature. After the oil gas produced in the dry distillation reactor is cooled down by condensation, the gaseous hydrocarbon compounds are separated therefrom, and then the different fractions are fractionated from the gaseous hydrocarbon compounds; gasoline and diesel oil fractions may be further processed to give gasoline and diesel oil mixture composition, light oil for chemical industry, fuel oil, aromatic products, etc; and the heavy oil fraction may be further thermally cracked to produce light oil, or it can be directly used to produce coal pitch. The distilled oil shale powder from the dry distillation reactor is delivered into the decarbonization reactor, into which adequate hot air is introduced and where the carbon is combusted to be completely removed. The flue gas is discharged after purification and energy recovery. The powder is stored after being cooled down, wherein the carbon content thereof is less than 0.5%.

The fluidized bed that can be used in the present invention is not specifically limited. Preferred fluidized bed reactor includes reactor riser, batch-type fluidization kettle reactor, bubbling-type fluidized bed reactor, and moving bed reactor. The most preferred one is reactor riser. There may be 2-4, preferably 2, reactor risers mounted depending on the nature of the raw material and the purpose product. Suitably, the top of the reactor riser has cyclone separator of 2-4 levels, in order to maximize the reduction of the fume discharge.

The reaction condition for the fluidized bed reactor according to the present invention is: the pressure of 0.1-0.6 MPa (normal pressure or increased pressure), the operation temperature of 400-800°C, the ratio of gas to solid of 1.0-20.0: 1(v/v) (preferably 2:1-10:1). Additionally, the temperature of the fluidized bed reactor for

decarbonization can be a little higher, for example, 500-800°C.

The grinding of the oil shale can be carried out by using conventional grinding devices. Typically, the grinding of the oil shale according to the present invention includes two stages, i.e. the breaking of the large block and the grinding.

First, large blocks of oil shale are broken into crushed aggregates with particle size of less than 5 cm, preferably less than 3 cm, by crushing machinery.

Next, these crushed aggregates are grinded into 50-300 mm powder by a fine grinding machinery such as Raymond mill and pneumatic crusher.

Deoiling by dry distillating may employ high temperature dry gas or high temperature steam as a heat carrier and medium for the delivery of powdered oil shale species. During dry distillating, the heavy shale oil may also be introduced and thermally cracked. The operation temperature of the dry distillation reactor is typically between 400-800°C.

The method according to the present invention can also be used to process solids containing carbon such as coal gangue. The processing scheme for processing the oil-containing coal is identical to that for processing oil shale. The deoiled and decarbonized solid substances are utilized comprehensively according to their different chemical compositions. Deoiling reactor may be omitted in the case of processing the coal gangue.

The shale oil produced by the method according to the present invention can further produce products with high added values, such as aromatics, gasoline fractions, diesel oil fractions, heavy shale oils and coal pitch.

The heavy shale oil produced by the method according to the present invention comprises the shale oil fraction of above 350°C, the fraction of 350-500°C, and/or the fraction therebetween. The heavy shale oil may be thermally cracked in the dry distillation reactor, or be used to produce coal pitch, preservative coatings, the fuel for firing the porcelain, etc.

Now, the present invention will be illustrated in detail together with the flow process chart 1.

The block oil shale 1 is grinded into powdered oil shale 3 by two-stage crasher 2, and then delivered into the dry distillation reactor 4. The high temperature dry gas 6 and heavy shale oil 7 entered into the dry distillation reactor 4 from the bottom thereof, and they are deoiled by dry distillating and thermally cracked, respectively.

The deoiled oil shale 8 is delivered into the decarbonization reactor 10. The high temperature air 11 enters the decarbonization reactor 10 from the bottom thereof, and

completely burns the residue carbon in the oil shale in fluidizing condition. The flue gas 9 is discharged from the top and released after purification and heat recovery. The deoiled and decarbonized oil shale 12 is discharged from the upper part and stored after being cooled down.

The oil gas 5 discharged through the top of the dry distillation reactor 4, after being cooled down, is delivered into fractionating tower 13, where the oil gas 5 is fractionated into tower top gas 14, gasoline fraction 15, diesel oil fraction 16, heavy shale oil 7, and coal pitch 17. In the gas separation tank 20, the fractionating tower gas 14 is separated into dry gas 6, discharged dry gas 18, liquefied gas 19 and condensate oil 21.

The main advantages of the present invention are: The fluidizing dry distillating of the oil shale and pyrolysis of the heavy shale oil are simultaneously completed in the same reactor, and the deoiled oil shale is decarbonized in another reactor. The shale oil can be used to produce products with high added values, such as aromatics, light oil for chemical industry and fuel gas, to make sufficient use of substances derived from the oil shale. The exhaust gas containing sulfur and nitrogen can be discharged after purification and energy recovery, therefore, it hardly causes environmental pollution. Upon using the system of energy recovery, the total energy of the system according to the present invention is excessive, and the excess energy can be delivered outside. The oil shale only needs physically grinding, without chemical treatment.

The invention is further illustrated by the following examples. These examples are only intended to illustrate the invention, but not to limit the scope of the invention. For the experimental methods in the following examples, they are performed under routine conditions, or as instructed by the manufacturers, unless otherwise specified. The percentage is by weight, unless otherwise specified.

Example 1

The oil shale from a certain place contains 10% of oil, up to 85% of kaolin (mainly aluminum oxide and silicon oxide), and 5% of carbon.

The process flow was two fluidized bed reactors in the form of reactor riser, one of which was a dry distillation reactor, the other was a decarbonization reactor. The heavy shale oil of above 400°C was introduced into the dry distillation reactor and

thermally cracked. There was a precipitator settled on the top of the reactor riser, which had two levels of cyclone separators, and a third level of cyclone separator before the flue gas entering the energy recovery part.

The process conditions were as follows:

1) The dry distillation reactor

the reaction pressure of 0.15 MPa (gauge pressure, corresponding to 1 atm plus 0.15 MPa), the reaction temperature of 500°C, the ratio of gas to solid of 4.0:1 (v/v).

2) The decarbonization reactor

the reaction pressure of 0.15 MPa (gauge pressure, corresponding to 1 atm plus 0.15 MPa), the reaction temperature of 680°C, the ratio of gas to solid of 4.0:1 (v/v).

3) Crashing

The oil shale was broken into crushed aggregates with the diameter of less than 3 cm by roller crusher, then grinded into 50-400 mm powder (with the average particle size of 150 mm) by high pressure milling machine.

4) Fractionating

A normal-reduced process was used.

The oil shale was grinded into 50-400 mm powder by two-stage grinding, then delivered by the dry air into the dry distillation reactor. The oil in the oil shale was gasified by dry distillating under the conditions described above, and meanwhile, the heavy shale oil is thermally cracked. The deoiled oil shale was delivered into the reactor riser for decarbonization by steam. The carbon in the oil shale was completely combusted under the conditions described above to become kaolin products (with carbon content of 0.2%) after being cooled down. The flue gas produced during the carbon combustion was energy-recovered by a flue machine, and then washed by saturated white lime water before discharge. The oil gas from the top of the dry distillation reactor was cooled down by condensation, then delivered into the fractionating tower and distilled, then cut. The distribution of the products was: the dry gas and liquefied gas: 20%; 65-180°C light oil for chemical industry: 40%; 180-350°C diesel oil admixture composition: 20%; heavy shale oil of above 350°C: 20%, wherein 10% of the heavy shale oil of above 350°C was delivered into the dry distillation reactor for thermal cracking, and the rest part was used as coal pitch products.

In this example, the energy recovery system itself not only provided energy to the system of the process, but also provided the excess energy to the outside.

Since the parent material of the oil shale is substantially the kaolin with high

quality, kaolin products with high quality were obtained by deoiling and decarbonization in this example. Some light oil for chemical industry, diesel oil admixture composition, liquefied gas, coal pitch, a small amount of aromatic products were simultaneously obtained. The final products included: kaolin with high quality, liquefied gas, light oil for chemical industry, diesel oil admixture compositions, and a small amount of coal pitch.

In comparison with the current fluidizing combustion method, the method according to the present invention mainly has the following advantages: more varieties of products obtained, the parent material of the oil shale being of good use, the high operation flexibility of the reactor riser process, and the smaller amount of fume discharge.

All the documents cited herein are incorporated into the invention as reference, as if each of them is individually incorporated. Further, it would be appreciated that, in the above teaching of invention, the skilled in the art could make certain changes or modifications to the invention, and these equivalents would still be within the scope of the invention defined by the appended claims of the application.